REMARKS

Applicant has amended his claims in order to further clarify the definition of various aspects of the present invention. Specifically, Applicant has canceled claim 31 without prejudice or disclaimer, and have added new claim 33 to the application. Claim 33, dependent on claim 20, recites that the processing solution etches the silicon oxide but does not etch the silicon wafer. Note, for example, the first full paragraph on page 6 of Applicant's specification.

Initially, Applicant respectfully requests that the present amendments be entered. Noting, for example, canceling of claim 31 without prejudice or disclaimer, it is respectfully submitted that the number of claims being considered on the merits in the above-identified application, subsequent to entry of the present amendments, is no greater than the number of claims finally rejected. In addition, noting, for example, arguments previously made by Applicant, as well as descriptions in Applicant's specification in the first paragraph on page 6 thereof, referred to previously, it is respectfully submitted that the present amendments clearly do not raise any new issues, including any issue of new matter. Noting the new grounds for rejection in the Office Action mailed July 29, 2002, it is respectfully submitted that the present amendments are clearly timely. In addition, noting that the present claim amendments further define a property of the processing solution, it is respectfully submitted that the present amendments materially limit issues remaining in connection with the above-identified application; and, at the very least, present the claims in better form for appeal.

In view of the foregoing, it is respectfully submitted that Applicant has made the necessary showing under 37 CFR § 1.116(c); and that, accordingly, entry of the present amendments is clearly proper.

Applicant respectfully traverses the rejection of his claims on prior art grounds, as set forth in the Office Action mailed July 29, 2002, and respectfully submits that all of the claims present in the above-identified application patentably distinguish over the teachings of the prior art applied in the Office Action mailed July 29, 2002, that is, the teachings of the U.S. Patents to Ohmi, et al., No. 5,990,060 (Ohmi '060), to Wang, No. 6,087,243, to Okutani, No. 5,135,608, to Hazama, et al., No. 5,162,880, to Hwang, No. 5,512,519, and to Ohmi, et al., No. 5,277,835 (Ohmi '835), under the provisions of 35 USC §103.

It is respectfully submitted that these references as applied by the Examiner would have neither taught nor would have suggested such a method of manufacturing a semiconductor integrated circuit device as in the present claims, including, *inter alia*, wherein the surface of a semiconductor wafer, covered with an insulating film whose main surface is mainly formed of silicon oxide, is cleaned using a processing solution which contains hydrogen peroxide, hydracid fluoride salt and water, with concentration of this salt being in a range of about 0.1 - 3 mol/l; and thereafter, removing the insulating film to expose the surface of the semiconductor wafer; and after removing the insulating film subjecting the silicon wafer to a heat treatment to form a gate oxide film over the silicon wafer. See claim 20.

That is, as set forth in claim 20, and as will be discussed further infra, it is respectfully submitted that these references do not disclose, nor would have suggested, wherein the surface of a semiconductor wafer covered with an insulating film whose main surface is mainly formed of silicon oxide is cleaned using the recited processing solution; and, thereafter, there is performed a step of removing the insulating film and thereafter forming a gate oxide film over the silicon wafer. It is emphasized that according to present claim 20 the step (b) of cleaning is performed using the recited

processing solution; and, thereafter, the insulating film is removed, and thereafter the step (d) of subjecting the silicon wafer to a heat treatment is performed to form the gate oxide film. Of course, since step (c) follows step (b) and step (d) follows step (c), the step (d) of forming the gate oxide film is performed after the cleaning of the surface of the silicon wafer using the recited processing solution.

Special problems arise due to the cleaning processing used, prior to forming the gate oxide film, when forming the gate oxide film. The present invention, using the recited processing solution at the time, in sequence, of performing step (b), avoids such problems.

In addition, it is respectfully submitted that the references as applied by the Examiner would have neither taught nor would have suggested such a method of manufacturing a semiconductor integrated circuit device as in the present claims, including, *inter alia*, the other aspects of the present invention as in the remaining, dependent claims, such as (but not limited to) wherein the processing solution, used in the cleaning step (b), etches silicon oxide but does not etch the silicon wafer (see claim 33); and/or wherein the hydracid fluoride salt is ammonium fluoride or tetraalkyl ammonium fluoride (note claims 21 and 22, respectively); or wherein the processing solution includes HF and HF_2^- as etching seeds of silicon oxide (note claim 23); or wherein the pH of the processing solution is in a range of 6-11 (note claim 26); or wherein a step of cleaning during ultrasonic vibration of the processing solution is performed (see claim 25); or temperature of the processing solution during the cleaning as in claim 27; or wherein the insulating film is removed by dipping in a mixed solution of hydrofluoric acid and water (see claim 28); or the additional drying step, after the insulating film is removed and prior to forming the gate oxide film (note claim 29), with the silicon wafer being immediately transferred to a chamber for forming the gate oxide

film, after drying (note claim 30); or the additional heat-treatment in an atmosphere of NO or N_2O, segregating nitrogen at the interface between the gate oxide film and the silicon wafer (see claim 32).

The present invention is directed to a method of manufacturing a semiconductor integrated circuit device, advantageously applied to a cleaning process for a silicon wafer in cleaning the wafer prior to forming a gate oxide film of the device.

In manufacturing a large scale integrated circuit device using a wafer made of mono-crystalline silicon, a so-called RCA wafer cleaning technique has been used, as described in the paragraph bridging pages 1 and 2 of Applicant's specification.

There is a desire to improve the RCA cleaning technique, and various attempts for improvement thereof have been made, as described on pages 2-4 of Applicant's specification. However, these proposed techniques have been insufficient, particularly in connection with forming an MOSFET which requires a thin gate oxide film of high quality. See the second full paragraph on page 4 of Applicant's specification. Note also the second full paragraph on page 4, and the paragraph bridging pages 4 and 5, of Applicant's specification, describing problems in connection with these proposed processing techniques. These problems are particularly serious in connection with forming a gate oxide of an MOSFET which requires a thin gate oxide film of high quality.

Against this background, Applicant provides a method having especially advantageous effects for cleaning a semiconductor wafer, in processing for forming a gate oxide film of a semiconductor integrated circuit device. Applicant has found that by utilizing a processing solution containing hydrogen peroxide, hydracid fluoride salt and water, the salt being included in a specified amount, for cleaning the surface of the silicon wafer covered with an insulating film whose main surface is mainly formed of silicon oxide; and with this insulating film thereafter being removed to expose the

surface of the silicon wafer; and the silicon wafer then being subjected to a heat treatment to form the gate oxide film, the cleaning can be performed at relatively low temperatures, and the silicon oxide film is cleaned and etched without etching the silicon substrate, so that contamination of the substrate can be avoided. Moreover, through use of the processing solution of the present invention, in processing steps leading up to and including the formation of the gate oxide film, the cleaning can be accomplished in a short time and at a low temperature, without deteriorating flatness of the wafer surface. Note, for example, the first full paragraph on page 6 of Applicant's specification.

Furthermore, through use of the further, oxy-nitrifying processing performed after forming the gate oxide film, nitrogen is segregated at the interface between the gate oxide film and the wafer, and this segregation of nitrogen at the interface moderates distortion at the interface which induces occurrence of hot carriers, thereby improving reliability of the gate oxide film. Note the paragraph bridging pages 18 and 19 of Applicant's specification.

Ohmi '060 discloses a cleaning method and a cleaning device which can remove foreign materials deposited on a substrate after removal of photoresist by plasma processing. See column 1, lines 6-10. This patent discloses that foreign materials can be removed under room temperature, by using a cleaning liquid which is a basic and water-soluble fluoride and an oxidizing agent, mixed in pure water. Note column 2, lines 20-29. See also column 2, lines 37-39 and 48-51; column 3, lines 42-47; and column 4, lines 45-50. This patent further discloses that by irradiating ultrasonic waves to the cleaning liquid or pure water, it is possible to improve the cleaning effect. Note the paragraph bridging columns 3 and 4 of this patent. This patent further discloses that the cleaning liquid can be applied not only to removal of photoresist, but also to removal

of various types of high polymer organic coating films such as paint or adhesive, films of machine oil, as well as removal of surface surfactant or dye or the like. See column 8, lines 24-34. Note also the paragraph bridging columns 2 and 3; and column 5, lines 7-10, of Ohmi '060. This patent, at the above-referred-to portion of column 8, specifically describes that the technique of Ohmi '060 is advantageously used for removing foreign materials deposited and remaining on the substrate even after a photoresist after ion injection and/or reactive ion etching processing used in a semiconductor production process or in the flat display panel production process.

It is emphasized that Ohmi '060 is primarily concerned with a cleaning liquid and cleaning method removing organic materials, particularly removal of photoresist. It is respectfully submitted that this patent is primarily concerned with removal of photoresist in connection with ion injection or reactive ion etching processes. It is respectfully submitted that this patent does not disclose, nor would have suggested, the presently claimed method, including performance of the recited cleaning using the specified processing solution, prior to and leading up to forming the gate oxide film, and advantages achieved.

Moreover, it is respectfully submitted that this applied reference does not disclose, nor would have suggested, use of the cleaning liquid disclosed in the patent, in processes, including the cleaning, leading up to and including formation of the gate oxide, or concentration of the hydracid fluoride salt in the processing solution as in claim 20.

It is emphasized that according to the present invention, the cleaning technique using the recited processing solution is a cleaning step prior to formation of the gate oxide film. Due to requirements of the gate oxide film, the present invention provides certain advantages, including wherein the surface of the silicon wafer is not etched.

See especially claim 33. Therefore, it is possible to remove contamination without deterioration of the flatness of the silicon wafer surface, for example, so that a gate oxide film with a high quality can be advantageously formed according to the present invention.

To the contrary, it is respectfully submitted that Ohmi '060 is concerned with a cleaning step after formation of the gate oxide film. It is respectfully submitted that the cleaning liquid of Ohmi '060 is directed to a cleaning after formation of the gate oxide and after removal of a photoresist mask, and would have neither taught nor would have suggested problems in connection with cleaning prior to forming the gate oxide film, as discussed in the foregoing, and overcoming such problems through use of the processing solution for cleaning as in the present invention.

Thus, it is respectfully submitted, as can be seen in the foregoing, that the purpose and requirements with respect to cleaning prior to formation of the gate oxide film are different from those with respect to cleaning after formation of the gate oxide film; and it is respectfully submitted that Ohmi '060 would have neither taught nor would have suggested the present invention, including cleaning using the recited processing solution as in the present claims, prior to formation of the gate oxide film, and advantages thereof.

The contention by the Examiner that Ohmi '060 "discloses only process steps (or conditions) necessary to clean a substrate utilizing the processing solution" (emphasis in original; see the paragraph bridging pages 4 and 5 of the Office Action mailed July 29, 2002) is noted. It is respectfully submitted, however, that Ohmi '060 does not disclose, nor would have suggested, use of the cleaning liquid therein prior to formation of the gate oxide film. Particularly in light of problems arising in connection with forming gate oxide films after cleaning, which problems are overcome by the present invention,

as discussed previously, the contention by the Examiner concerning obviousness with respect to Ohmi '060 describing use of a processing solution in a cleaning process, in general, is respectfully traversed.

It is respectfully submitted that, in the involved art, different cleaning solutions are used prior to, and subsequent to, forming the gate oxide film. In connection therewith, note the enclosed Table 7 on page 254 of the publication Cleaning Technology for Silicon Wafer Surface (February 28, 1995). This shows that different cleaning solutions are used in cleaning prior to and after formation of the gate oxide. It is respectfully submitted that this publication provides further evidence that one of ordinary skill in the art concerned with in Ohmi '060 would not have utilized the cleaning liquid described therein, in a cleaning step prior to formation of the gate oxide film.

It is respectfully submitted that the remaining references as applied by the Examiner would not have rectified deficiencies of Ohmi '060, such that the presently claimed invention as a whole would have been obvious to one of ordinary skill in the art.

Wang discloses a method of manufacturing a semiconductor device including trench isolation. In a description of background art, this patent discloses a trench isolation technique including wherein, after the trench has been formed and filled, heating is utilized to densify the trench fill; and the remaining portion of the pad oxide layer is then removed with dilute hydrofluoric acid, followed by an industrial standard "RCA" clean, with a high quality gate oxide then being grown, followed by polysilicon deposition. Note, column 2, lines 9-41. This patent discloses a method of manufacturing a semiconductor device having an active region isolated by an insolation trench, including formation of a second oxide layer, as described in column 3, lines 32-63. This patent discloses that in accordance with the method described therein, a first sacrificial oxide layer is removed, as by etching with dilute HF followed by a surface

cleaning treatment commonly referred to as the "RCA" clean, as with a mixture of hydrogen peroxide and ammonium hydroxide or a mixture of hydrogen peroxide and hydrogen chlorite. A second sacrificial oxide is removed, as by etching employing a dilute HF dip followed by the standard "RCA" clean, exposing a fresh silicon surface, with a thin gate oxide layer being formed on this fresh silicon surface. Note from column 4, line 66 to column 5, line 28.

Initially, it is noted that according to Wang, the sacrificial oxide layer is removed, and thereafter a surface cleaning treatment is performed. It is respectfully submitted that this disclosure, even in combination with the teachings of Ohmi '060, would have neither taught nor would have suggested, and would in fact have taught away from, a process wherein the cleaning of the surface using the processing solution is performed, and thereafter the insulating film is removed and thereafter the gate oxide film is formed. That is, while Wang initially removes the pad oxide film and thereafter performs a cleaning, the present invention cleans and thereafter removes the insulating film. Clearly, the teachings of Wang, in combination of the teachings of Ohmi '060, would have taught away from the presently claimed subject matter including wherein cleaning is performed using the recited processing solution, removing the insulating film after the cleaning thereby to expose the surface of the silicon wafer; and after such removing, subjecting a silicon wafer to a heat treatment thereby to form a gate oxide film over the silicon wafer, and advantages thereof as discussed in the foregoing.

The contention by the Examiner that both Wang and Applicant are utilizing a common practice, set forth in the last three lines on page 5, and the first four lines on page 6, of the Office Action mailed July 29, 2002, is respectfully traversed. That is, it is emphasized that according to Wang the "RCA" clean is performed after removal of the sacrificial oxide. Such procedure as in Wang would have taught away from the

presently claimed process, including wherein the cleaning is performed and thereafter the insulating film is removed.

Okutani discloses thin film-forming technology and etching technology in processing wafers used for semiconductor devices. The patent describes a method of producing semiconductor devices including dry and wet processing steps for the wafers, and a step for carrying wafers between the dry and wet processing steps, the dry and wet processing steps and carrying step being continuously carried out in a predetermined atmosphere shutting off the open air. See column 2, lines 26-34. Note also, column 2, lines 42-54; and column 3, lines 57-64.

Even assuming, *arguendo*, that the teachings of Okutani were properly combinable with the teachings of Ohmi '060 and Wang, such combined teachings would have neither disclosed nor would have suggested the cleaning, removing and gate oxide film forming steps in the recited sequence as in the present claims, with the cleaning using the processing solution as recited in the present claims, and the advantages of this process as discussed previously.

Ohmi '835 discloses a surface treatment agent for use in fine surface treatment which is very effective for wet etching of silicon oxide film in the manufacturing process of semiconductor devices, as well as cleaning of fine-treated semiconductor devices. See column 1, lines 12-18. The surface treatment agent includes a mixed solution of fluoric acid, ammonium fluoride and water, the mixed solution containing specified amounts of hydrogen fluoride and ammonium fluoride. See column 3, lines 17-23.

Even assuming, *arguendo*, that the teachings of Ohmi '835 where properly combinable with the teachings of Ohmi '060 and Wang, as applied by the Examiner, it is respectfully submitted that the combined teachings of these references would have neither taught nor would have suggested the sequence of processing steps, including

the cleaning step, insulating film removing step, and gate oxide film forming step, with the cleaning step using the processing solution as in the present claims, and advantages thereof, as discussed previously.

Hazama, et al discloses a nonvolatile memory cell that is capable of being electrically written, read and erased, and a method of manufacturing this memory cell. A specific example of manufacturing the memory cell is set forth. See, for example, column 4, lines 32ff (note particularly column 4, lines 32-44).

Hwang discloses methods of forming silicon insulating layers in semiconductor devices, in which an oxide layer is formed by regulating the flow of NO and O_2 gas instead of an O_2 gas in a reaction chamber, so that nitrogen may penetrate into a Si and SiO_2 interface in order to improve the reliability of the semiconductor device. Note column 1, lines 6-13.

Even assuming, *arguendo*, that the teachings of Hwang and Hazama et al were properly combinable with the teachings of the other references as applied by the Examiner, it is respectfully submitted that such combined teachings would have neither disclosed nor would have suggested the presently claimed invention, including, *inter alia*, the sequencing of processing steps including cleaning the surface of the silicon wafer using the recited processing solution, thereafter removing the insulating film and after removing the insulating film subjecting the silicon wafer to a heat treatment to form a gate oxide film over the silicon wafer, and advantages thereof as discussed in the foregoing.

In addition, it is respectfully submitted that the teachings of the applied prior art would have neither disclosed nor would have suggested the other aspects of the present invention as in the remaining claims presently in the application, and advantages thereof as discussed previously.

In the paragraph bridging pages 4 and 5 of the Office Action mailed July 29, 2002, the Examiner notes various processing steps described by Wang. However, it must be emphasized that Wang discloses "RCA" cleaning, after removal of the respective sacrificial oxide layers. In the analysis by the Examiner of Wang, the Examiner does not even refer to the sequencing of removal of the sacrificial oxide layer. It is respectfully submitted that, properly construed, the combined teachings of Wang and of Ohmi '060 would have neither disclosed nor would have suggested the present invention.

Reference by the Examiner to Okutani in connection with claim 26, in the first line on page 7 of the Office Action mailed July 29, 2002, is not understood. It is emphasized that the Examiner has not applied Okutani in connection with claim 26; note the first two lines of Item 2 on page 2 of the Office Action mailed July 29, 2002. See in re Hoch, 166 USPQ 406, 407n.3 (CCPA 1970). Accordingly, it is respectfully submitted that the Examiner cannot use the teachings of Okutani in connection with the subject matter of claim 26, as in the Office Action mailed July 29, 2002.

The contention by the Examiner in Item 7 on pages 11 and 12 of the Office Action mailed July 29, 2002, that Ohmi '060 "discloses a critical aspect of the current invention, i.e., Ohmi ['060] discloses a processing solution as currently claimed", is noted. However, it is respectfully submitted that the present claims are directed to a process having recited processing steps, the last recited processing step including subjecting the silicon wafer to a heat treatment after removing the insulating film, thereby to form a gate oxide film over the silicon wafer; and wherein prior to removing the insulating film the silicon wafer surface is cleaned using a specified processing solution. Properly construing the presently claimed subject matter as a whole, rather than merely focusing on the processing solution, it is respectfully submitted that the

teachings of the applied references would have neither taught nor would have suggested the presently claimed invention.

The contention by the Examiner in the sentence bridging pages 11 and 12 of the Office Action mailed July 29, 2002, is noted. However, it is respectfully submitted that the Examiner has ignored unique problems arising in connection with cleaning prior to formation of the gate oxide film, as discussed previously and as described in Applicant's specification. Properly construed, it is respectfully submitted that, taking the present invention as a whole, the teachings of the applied prior art would have neither disclosed nor would have suggested the presently claimed subject matter.

In view of the forgoing comments and amendments, entry of the present amendments, and reconsideration and allowance of all claims remaining in the application, are respectfully requested.

To the extent necessary, Applicants petition for an extension of time under 37 CFR 1.136. Please charge any shortage in fees due in connection with the filing of this paper, including extension of time fees, to the Deposit Account No. 01-2135 (Case No. 843.37558VX1) and please credit any excess fees to such Deposit Account.

Respectfully submitted,

ANTONELLI, TERRY, STOUT & KRAUS, LLP

By _____
William I. Solomon
Reg. No. 28,565

Attachment: Table 7

WIS/sjg:dlt
Tel. No.: (703) 312-6600
Fax No.: (703) 312-6666

シリコンウェーハ表面のクリーン化技術

柏木 正弘／服部 毅 編著

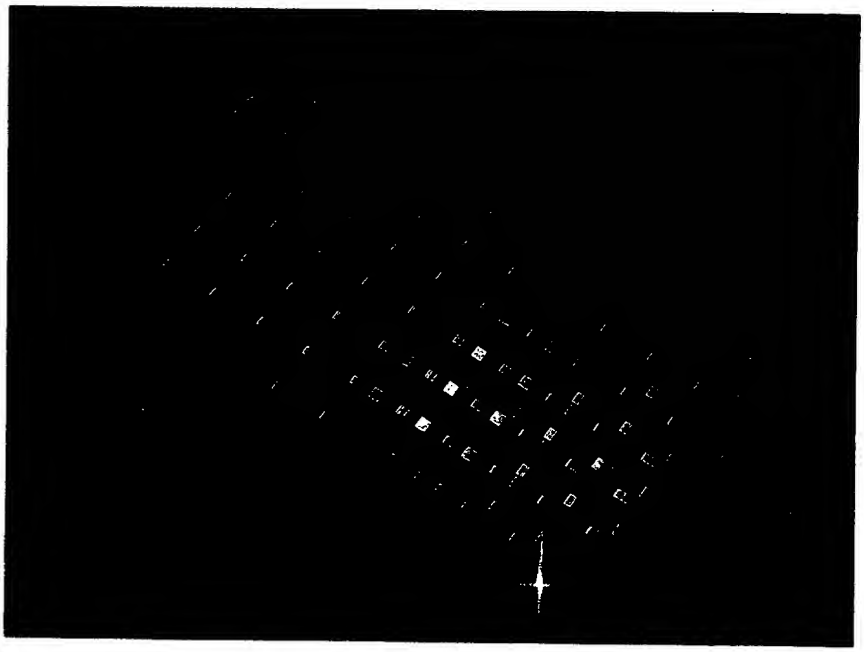

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表-7 標準的RCA洗浄法[12)]

Hydrogen peroxide-based immersion cleaning procedures for silicon wafers

A. Preliminary cleaning (if necessary)

1. Remove bulk of photoresist film (if present) by plasma oxidation stripping, or immersion in organic photoresist stripper, or with a hot 1:2 v/v H_2O_2-H_2SO_4 mixture if adequate safety[23] precautions are exercised.

2. Rinse with wafer (see note on water purity for entire processing).

3. Transfer the wafers to a clean Teflon® holder. Pick up wafers with Teflon® or polypropylene plastic tweezer.

B. Removal of residual organic contaminants and certain metals (SC-1)

1. Prepare a fresh mixture of H_2O-NH_4OH-H_2O_2-(5:1:1) by measuring the following reagents into a beaker of fused silica (opaque silica ware is acceptable) :
   a. 5 volumes of water
   b. 1 volume of ammonium hydroxide (29%, electronic grade, w/w% based on NH_3)
   c. 1 volume of hydrogen peroxide (30%, unstabilized electronic grade w/w%)

2. Stir the solution with a clean rod of fused quartz.

3. Submerge holder with wafers in the cold solution and place the beakers on a hotplate.

4. Heat to 75 to 80℃. Then reduce heating to maintain the solution at 80℃ for an additional 10 minutes. (The vigorous bubbling is due to oxygen evoluation. Make sure not to boil the solution so as to prevent rapid decomposition of the H_2O_2 and volatilization of the ammonia.)

5. Overflow-quench the solution by placing the beaker under running wafer for about one minutes.

6. Remove holder with wafers and immediately place it in a cascade water rinse tank for 5 minutes.

C. Stripping of thin hydrous oxide film (1:50 HF-H_2O)

1. Submerge wafer assembly from step B.6 directly in an agitated mixture of 1 volume hydrofluoric acid (49%, electronic grade) and 50 volumes of water.

2. Allow to remain in the solution for only 15 seconds. Exposed silicon (but not SiO_2) should repel the HF solution[24]. Use a polypropylene beaker for this step.

3. Transfer the wafer assembly to a water tank, but rinse for only 20 to 30 seconds with agitation to remove the HF solution (this minimizes regrowth of a hydrous oxide film).

4. Transfer the wafer assembly immediately, without drying, into the hot SC-2 solution of step D.

D. Desorption of remaining atomic and ionic contaminants (SC-2)

1. Prepare a fresh mixture of H_2O-HCl-H_2O_2 (6:1:1) by measuring the following reagents into a beaker of fused quartz :
   a. 6 volumes of water
   b. 1 volume of hydrochloric acid (37% electronic grade)
   c. 1 volume of hydrogen peroxide (30%, unstabilized, electronic grade)

2. Place the beaker on a hotplate and heat to 75 to 80℃.

3. Submerge the still-wet wafers in the holder (after step B.6 or C.3) in the hot solution.

4. Maintain the solution at 80℃ for 10 to 15 minutes.

5. Overflow-quench as in step 8.5.

6. Continue the rinsing at this stage for a total of 20 minutes in a cascade rinsing system.

E. Drying of the wafers

1. Transfer the holder with the wet wafers into a wafer centrifuge.

2. Apply a final water rinse during spinning.

3. Allow to dry while gradually increasing the spinning speed (to avoid aerosol formation from the water droplets).

4. Remove the wafers by dump transfer for high-temperature processing. If single-wafer handling must be used, handle the wafers only at the edge with plastic tweezers.

F. Storage

1. Avoid storage of cleaned wafers. preferably by immediate continuation of processing. If storage is unavoidable. store the wafers in closed glass containers cleaned with hot SC-1 solution, followed by water rinsing and over-drying.

Note concerning processing water and reagents
All water used for preparing the reagent mixture or for rinsing should be thoroughly deionized and ultrafiltered, with a resistivity in the 10 to 20-megohm range at 18 to 23℃. All reagents should be electronic grade, preferably ultrafiltered for freedom from particulate impurities.